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Development of Green Nickel-Based Zeolite Catalysts for Citronella Oil Conversion to Isopulegol

S. Tursiloadi[a], A. A.Litiaz[b], R. Pertiwi[a], I. B. Adilina[a] and K.C. Sembiring[a]*

[a]*Research Centre for Chemistry, Indonesia Institute of Sciences, Kawasan PUSPIPTEK Serpong, Tangerang, 15314, Indonesia*
[b]*Faculty of Science and Technology, State Islamic University Syarif Hidayatullah, Jln. Ir. H. Juanda No. 95 Ciputat,Tangerang, Indonesia*

Abstract

Derivatization of citronellol, citronellal and geraniol into fine chemicals such as isopulegol, hydroxyl citronellal, menthol, geranial esters, esters citronellal and others will escalate the added value of citronella oil. Some products derived from essential oils are widely used for food and fuel additives, pharmaceuticals, cosmetics and perfumes. The synthesis of isopulegol from citronellal was studied on nickel-based zeolite catalysts. The citronella oilwas obtained by vacuum fractional distillation of lemongrass oil. The catalysts were prepared by supporting nickel on natural zeolite from Bogor (ZAB) by impregnation method with variations thenickel loading amount. Catalytic reactions were carried out at 200 ^{o}C under 2 Mpaof H_2 pressure for 3 h and it was also varied of catalyst weight amount.The products distribution was found to depend on the catalyst weight. The Ni/ZAB 20% of metal loading catalyst (5 % weight) was highly active and selective towards isopulegol (100% conversion and 57% selectivity).

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*Keywords:*Citronella oil; citronellal; natural zeolite; isopulegol.

* Corresponding author. Tel.: +62-21-7560 929; fax: +62-221-7560 59.
*E-mail address:*kiky001@lipi.go.id

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Nomenclature

B	Brönsted acid
BET	Brunauer, Emmett nd Teller
CL	Calcination
CLHT	Calcination followed by hydrogen treatment
Bpy	Brönsted acid by pyridin adsorbtion
DSC	Differential Scanning Calorimetry
FTIR	Fourier transform infrared spectroscopy
HT	Hydrogen treatment
MPa	Mega Pascal
Lpy	Lewis acid by pyridin adsorption
TGA	Thermal Gravimetric Analysis
XRD	X-ray diffraction
ZAB	Natural Zeolite from Bogor

1. Introduction

According to the geological position, Indonesia essentially has abundant source of natural zeolites. At least 50 sites have been known to contain zeolite minerals such as Sumatra, Java, Bali, Nusa Tenggara, Sulawesi, Maluku, and Irian Jaya. Zeolites play important roles as acidic solid catalysts in several industries, especially petroleum refining and petrochemical industry. Although zeolites highly potential material to reduce industrial production cost as catalyst, their modification to improve catalytic performance has been less explored.

Zeolite is a natural mineral porous alumina silicate (~ 2 nm) that is composed of tetrahedral alumina (AlO_4^{5-}) and silica (SiO_4^{4-}) which has activity site and high thermal stability[1]. The negative charge generated by substitute Si to Al in the zeolite framework neutralized by cations which are bound weakly. There are two types of zeolites, natural zeolite and synthetic zeolite. Natural zeolite contains cations K^+, Na^+, Ca^{2+} or Mg^{2+} while synthetic zeolite contains only cations K^+ or Na^+. When thecationsinthe form ofprotonsframework, theBrønstedacidsitesare formedandmodifiedzeolitesbecomeacidicsolidcatalyst, as can be seen in Fig. 1[2,3].

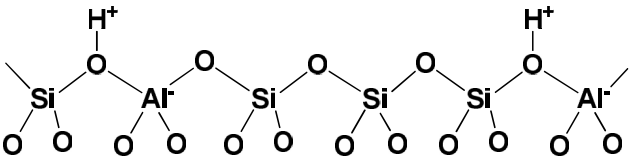

Fig. 1.Chemical structure ofzeolitewith Brønstedacidsites

Zeolite is very unique, it has a hollow structure that is usually filled with water and cations that can be exchanged, and hasspecificpore size also nature of the physico-chemical properties which are very important for catalyst application. Zeolite also canbe employed as ion exchangers absorbent and it perform highly selective catalyst activity forspecific reaction[4]. Therefore, many researchers develope zeolites as a support for heterogeneous catalysts by modifying their catalytic active sites which distribute uniformly on most of the solids, their empty spaces structure and canals that are easily reached by reactant molecules.

Various studies have reported the use of acid catalyst, such as SiO_2, Al-MCM-41, $ZnBr_2$ for cyclization of citronellal. The Brønstedacidwas able to increase the rate of isomerization of citronellal although the formation of isopulegol was still low. Meanwhile, Ni also has been reported to enhance the surface acidity of zeolite due to the metal atom deposite on the exterior zeolite surface, each reduced metal atom would have electron donor/acceptor properties and could introduced extra protons into the structure[5].

One of the citronella oil derivatives, isopulegol, is an intermediate product of menthol production which is the one of worldwide important flavors for many industries such as pharmaceutical and fragrance industries. Now,most researchers have investigated various catalysts with Brønstedacid sites and Lewis acid sites, for the example Arvela*et.al*who conducted cyclization reaction of (R)-(+)-citronellal to (S)-(-)–isopulegol[6]. Applying several catalysts, they found that β-zeolitehas the best catalyst toproduceisopulegol. Cyclization reaction of citronella oil to isopulegol shown in Fig. 2.

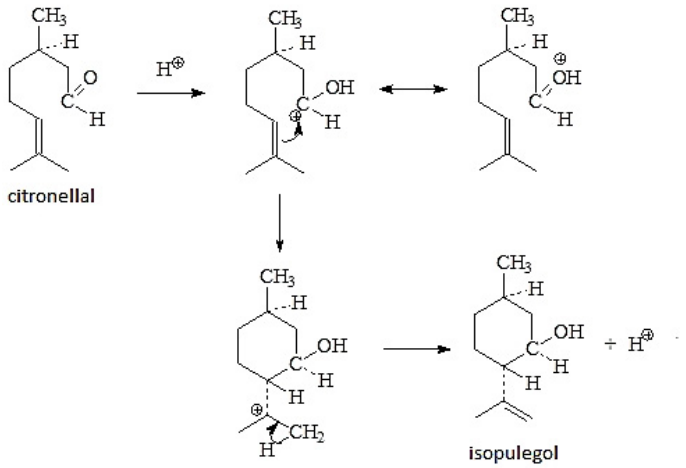

Fig. 2. Mechanism of citronellal cyclization[7]

In this work, the preparation of heterogeneous green nickel-based natural zeolite catalysts from Bogor was studied. This catalysts were applied in cyclization reaction of citronella oil to isopulegol. Nickel-based zeolite catalysts are considered more economical than other synthesized silica-alumina catalystdue to these materials are abundant and readily available.

2. Materials and Methods

2.1. Raw materials

Zeolite used in the experiments was supplied from PT. Atsirindo Indonesia, Bogor (particle size: 325 mesh). Catalyst precursor is nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$), ethanol 96%, hydrochloric acid (HCl) were commercial product from Merck and were used as received. The citronella oil was obtained by vacuum fractional distillation of *Cymbopogon nardus* plants(distillate fractions DF-33, P = 80mbar, R = 20/10).

2.2. Catalyst preparation

Natural zeolite first was acidifiedby adding 50 grams of natural zeolite to 100 mL of HCl 1M in 250 mL beaker glass. The mixture was stirred at room temperature for 1 h, following by filtration and washing with distilled water until pH neutral. The sample was then dried at 250 °C for 3 h and named as ZAB.

Nickel-based zeolite catalysts were prepared via impregnation method by adding 1 g (10% metal loading) or 2 g (20% metal loading) nickel in the form of $Ni(NO_3)_2.6H_2O$ salt into 30 mL of 96% ethanol. Amount of 10 g of ZAB was added to the solution and stirred at 80 °C until the solvent was fully evaporated. Then, the sample was dried at 100 ^oC for 2 h. The catalysts was divided into two parts, the first part would not be calcined and the second part would be calcined at 500^oC for 2 h. The heterogeneous catalysts were named as Ni/ZAB.

2.3. Catalyst characterization

XRD patterns were recorded using MAC Science MXP3 V, operated at 40 kV and 15 mA, using Cu Kα radiation with λ1 = λ2 = 1.54059 Å and 1.54441 Å. Samples were scanned at 5º to 80º 2θ using a step size of 2θ = 0:02 and a time per step of 0:24 s. The textural characteristics, such as BET specific area and pore volume (BJH method), were determined by N_2 adsorption–desorption on a Micromeritics TriStar II 3020 instrument. Prior to the analysis the samples were outgassed for 3 h at 250^oC.Brönsted and Lewis acid sites were observed by FTIR with pyridine as a probe molecule. Samples were pressed into small discs and placed in the IR cell. All infrared spectra were collected data resolution of 4 cm^{-1} in the 4000-400 cm^{-1} range.The decomposition of catalysts were investigated by thermal gravimetric analysis (TGA) using Linseis STA PT 1600 analyzer under heating rate of 10°C min^{-1}.

2.4. Catalytic test and product analysis

Catalystactivityforisopulegolsynthesisfrom citronella oil was carried out in a 20 mL autoclave. The catalyst was

reduced first before utilized by heated at 300°C under H_2 flow for 2 h. An amount 1 g of citronella oil was introduced to the autoclave, then 5% or 10% of Ni/ZAB was also added into it. The reaction was occured at 200 °C under H_2 constant pressure of 2 Mpa for 3 h. Reaction products were analyzed by GC-Mass spectroscopy (Agilent 19091S, column HP-5MS (30 m x 250 µm, 0.25 µm)).

3. Results and Discussion

3.1. Catalyst characterization

3.1.1. TG-DSC analysis

Physical properties of the catalyst Ni/ZAB 10% and Ni/ZAB 20%, the mass change of the materials as a function of temperature and time, and also the heat flow change associted with phase transition or reaction are investigated by TG-DSC as shown in Fig. 3. It can be seen for both catalysts, the initial exothermic peak at around 80 °C that might be attributed to moisture on the surface. For Ni/ZAB 20%, the weight decline sharply by 14% until temperature reach 580°C with exothermic peak at temperature 200°C, 260°C and 500°C. For Ni/ZAB 10%, a sharp decline of the weight by around 17% at temperature range of 100 °C to 520 °C with an exothermic peak at 480 °C. This might revealed the release of crystal water and the burn out of organic compounds. Increasing weight of catalyst after 700 °C indicates the Ni metal undergoes oxidation with oxygen from the air to form a binding Nickel oxide (NiO)[7].There was no appreciable thermal changes and weight loss when the samples were heated above 500 °C and it was considered as calcination temperature of the catalysts.

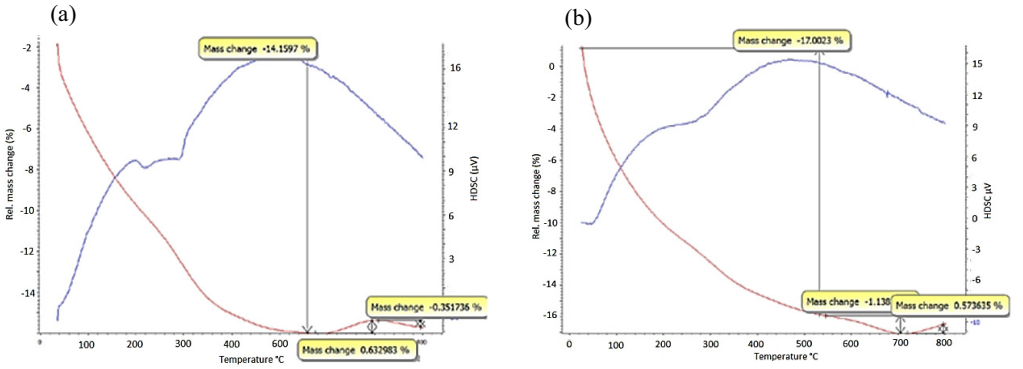

Fig.3.TG-DSC curve forcatalyst(a) Ni/ZAB20% (b)Ni/ZAB10%

3.1.2. Surface area analyzer measurement

Surface area analysis was conducted to determine the surface area of the material, pore distribution of material and a gas adsorption isotherm on a material[9]. The surface area, volume, pore size of the various nickel-based zeolite catalysts were measured the surface area analyzer according to the BET method that is presented in Table 1.

Table 1. Results of analysis with BET method SAA

No.	Name of Samples	Specific surface area BET (m^2g^{-1})	Pore Volume (cm^3g^{-1})	Pore Diameter (nm)
1	ZAB	77.94	0.006	2.07
2	Ni/ZAB 10wt%	21.17	0.003	2.08
3	Ni/ZAB 10wt% CL	31.20	0.004	2.08
4	Ni/ZAB 10wt% CL-HT	29.13	0.003	2.08
5	Ni/ZAB 10wt% HT	19.09	0.004	2.07
6	Ni/ZAB 20wt%	17.35	0.003	2.08
7	Ni/ZAB 20wt% CL	29.37	0.004	2.08
8	Ni/ZAB 20wt% CL-HT	29.46	0.003	2.08
9	Ni/ZAB 20wt% HT	37.09	0.005	2.08

Note: CL= Calcination, HT: Hydrogen Treatment

The specific of surface area activated ZAB was 77.94m^2g^{-1}. The addition of Ni metal decreases its surface area and total pore volume. It means that the impregnated nickel species might be cover the pore of the zeolite support and reformactive sites located in these pore metal sites.However, the average pore diameters of Ni/ZAB catalysts are

increased after calcination and reduction processes. Some of impurities on micro-pore of the zeolite was vanished after calcination process and Ni metal complex was changed to Ni oxide (NiO)[10].The pore structure variation may be derived from the support crystalline phase change under high temperature.

3.1.3. Adsorption of Pyridine characterization

The easiest and commonly method of distinguishing between Brönsted and Lewis acid species is the IR spectroscopy of pyridine chemisorption.Upon interaction with a Brönsted (B) acid, pyridine is protonated and absorbs at a specific IR wavelength around 1540-1545 cm^{-1}(Bpy) and Lewis (L) acid at 1450-1455 cm^{-1} (LPy) respectively[11].

Acidity of Ni/ZAB catalysts are showed in Table 2. The FTIR spectra in Fig 4 presented that the spectrum of pyridine was appeared at 1640 cm^{-1} and 1540 cm^{-1} indicating the formation of Bronsted acid sites.

Table2. Results of adsorption of pyridine

No.	Sample name	Adsorbed Pyridine	Acidity
1	ZAB	0.0523	1.3021
2	Ni/ZAB 10wt%	0.0254	0.6404
3	Ni/ZAB 10wt% CL	0.0157	0.3978
4	Ni/ZAB 10wt% CL-HT	0.0242	0.5859
5	Ni/ZAB 10wt% HT	0.0179	0.4380

Spectrum of zeolite also showed at 750-800 cm^{-1}, 1000-1250 cm^{-1} and around 3500 cm^{-1} (Fig. 4). In the IR-spectrum of Ni/ZAB catalysts, the characteristic bands of Si-O and Al-O are observed at 750-800 cm^{-1}. The other bandsbetween 1000 $cm^{-1}$and 1250 cm^{-1} indicates the internal texture of the zeolite in the form of asymmetric stretching vibration of Si-O and Al-O. Spectra of about 3500 cm^{-1} indicated of Si-OH stretching vibration.

3.1.4. X-Ray Diffraction analysis

X-ray diffraction pattern was commonly used to determine crystallinity, size, and the phase of the zeolite. This method can also detect the effect for the structure of zeolite as a result of the modification processes such as impregnation or calcination. Characterization of the crystal structure of natural zeolite before and after impregnation with nickel metal using XRD instrumentation shown in Fig 5.

According to the diffraction of catalysts,mordenite phase(2θ =9.84°, 13:48°, 22:34°, 25.74°, 26.66°, 27.68°) andclinoptilolite phase (2θ =11.2°, 19.72°, 22:42°, 25.82°, 27.92°) were detected inthe structure ofnaturalzeolite based on JCPDS data. The highestpeakat2θ=26.66°indicatesthat thenatural zeolite used in this studyis mainly composed ofmordenite with some presence of clinoptilolite phase. There is no change in the value of 2θ after ZAB modified.This showed diffraction also showed that calcination and impregnation didnot destroy the crystalline structure of the zeolite.

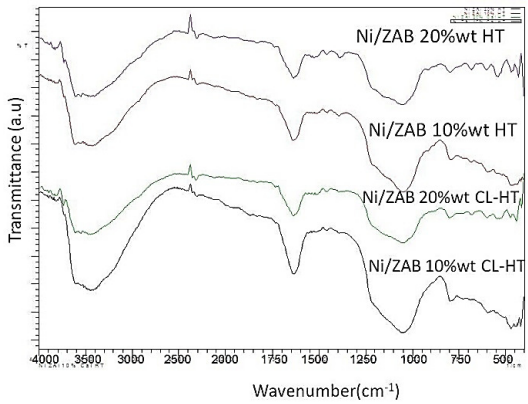

Fig 4. FTIR spectra of absorbed pyridine

Immobilization of catalysts with Ni metal increase the intensity of these peaks. However, it can be assumed that calcination process can remove some ofimpurities in theframework of zeolite and improve the crystallinity of zeolite structure. Ni metal might highly dispersed on the structure of Ni/ZAB-20wt% CL-HT and Ni/ZAB-20wt% HTsince Ni and NiO phase were not detected in the diffractogram.

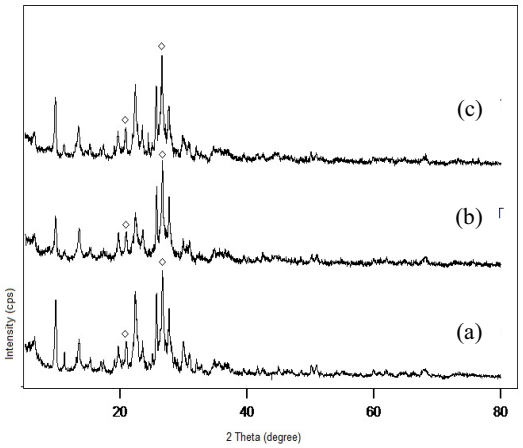

Fig 5. XRD patterns of (a) ZAB, (b) Ni/ZAB-20wt% CL-HT, (c) Ni/ZAB-20wt% HT.

3.2. Catalytic Activity

Cyclization of citronella oil was performed using Ni/ZAB catalysts series at 200°C for 3h with 2 MPa H_2 pressure. Isopulegol is an intermediate compound in the production of menthol which can be produced from the cyclization of citronellal with the presence of an acid catalyst. The high acidity of the catalyst would destabilize the C=C and C=O bond of citronellal where there is an interaction between electrons on the carbonyl and π electrons on the C=C bond with the Lewis acid site catalyst accompanied by protonation of the Bronsted acid to form isopulegol. Fig. 6 shows the possibilities of citronellal conversion steps: (i) isomerization/cyclization of citronellal to isopulegol or (ii) hydrogenation of citronellal to citronellol. Chuah *et al.*[11] reported that catalytic materials containing strong Lewis and weak Brønsted acidity show good activity and selectivity for cyclization of citronellal to isopulegol.

Table 3. Theresults ofGC-MS analysis

Catalysts	Catalyst weight (% wt)	Conversion (% Area)	Yield Isopulegol (% Area)	Yield Citronellol (% Area)	Yield Others (% Area)	Selectivity of isopulegol (%)
ZAB	5	100	12	0	88	12
	10	100	0	0	100	0
Ni/ZAB 10wt% CL-HT	5	100	40	0	60	40
	10	100	31	0	69	31
Ni/ZAB 10wt% HT	5	100	33	1	66	33
	10	100	9	0	91	9
Ni/ZAB 20wt% CL-HT	5	100	57	1	42	57
	10	100	18	1	81	18
Ni/ZAB 20wt% HT	5	100	41	4	55	41
	10	97	7	5	85	7

Reaction conditions: 1 g of oil of citronella, H_2, 2 MPa, 200°C, 3 Hours, CL: Calcination, HT: Reduction.

Analysis resultsusingGCMSinstrumentation shown inTable3. The catalytic activity was first tested with ZAB as catalyst and 12% yield of isopulegol (100% conversion) was obtained. According to the results,it can observedthat almost all of the catalyst can converted more than 97% of citronella oil. Ni/NZB-20wt%-HT with 10% amount of catalysthas the lowest activity to produceisopulegolcompoundswith only 7% of selectivity. In the other hands, increasing yield of isopulegol (57%) was showed by using Ni/ZAB 20wt% CL-HT catalyst with following a reduction of catalyst amount (5% weight). The activity and selectivity for the formation of isopulegol from citronellal on Ni/ZABcatalysts are significantly improved on the sample because: i) the citronellalcyclization rates increase with the surface concentration of acid sites; ii) the decreasing coverage of the support by Ni diminishes the formationof undesirable byproducts on surface metal sites.

In this study, the effect of Ni loading in the catalyst was observed at 10wt% and 20wt%. The product distributions changed slightly with increasing of the Ni loading for conversion. The presence of Ni metal will involve the formation of isopulegol. Some of citronella compound can react to form hydrogenation products such as citronellol, menthol, or 3,7-dimethyl octanol (Fig 6.).

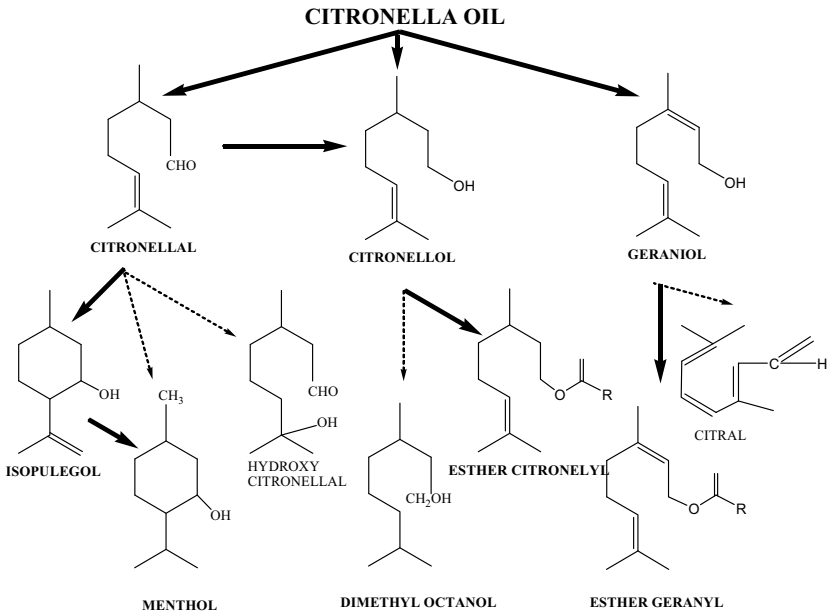

Fig 6. The reaction mechanism of citronella oil derivative

4. Conclusion

The Ni/ZAB catalysts can play role as a catalyst for cyclization of citronellal to isopulegol. These catalysts were prepared from natural zeolite (ZAB) by acid activation and immobilization of Ni using impregnation method. Ni/ZAB-20wt%-CLHT catalyst showed the highest activity of 100% conversion which yielded 57% of menthol and 57% selectivity. Both effect of Ni loading and amount of catalyst was investigated. A lower catalytic activity was seen for the Ni/ZAB-20wt%-HT catalyst (7% yield of isopulegol) when amount of catalyst is 10%. Then, Ni/ZAB catalysts are promising materials for utilization of citronella oil to flavor chemical like isopulegol.

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